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CHEMICAL & ENGINEERING

NEWS

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Water Treatment Chemicals

Regulations on contaminants drive product sales, development Page 17

News of the Week

■ Biomass burning is more widespread and dangerous to the environment than was previously thought, according to scientists attending first international conference dealing with this issue. **Page 4**

■ Report released last week by the Defense Department describes plans for developing 20 technologies critical to national defense. **Page 5**

■ New series of ruthenium-based catalysts provide very high activity and selectivity in converting methane to synthesis gas. **Page 5**

■ Perkin-Elmer has sold its electron-beam semiconductor fabrication business to Etec Corp. (a new firm formed from P-E employees), with five other firms participating in purchase. **Page 6**

■ Report by coalition of farm and environmental groups criticizes efforts to produce herbicide-tolerant crops through biotechnology. **Page 6**

Cover: Technician samples industrial effluent stream. Photo courtesy of Interco

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Business

Canada may soon have three methyl *tert*-butyl plants, one each in the Alberta, Quebec, and Ontario provinces. **Page 9**

Government

New proposals to levy taxes on pollutants are being studied by House committee. **Page 11**

Factors affecting the completion of a global chemical arms ban are considered during recent AAAS symposium. **Page 12**

Libyan chemical plant, an alleged site of chemical weapons production, damaged in fire. **Page 13**

Science/Technology

Shortage of acetonitrile has begun to hurt research laboratories as well as the petrochemical and pharmaceutical industries. **Page 15**

Efforts to monitor coastal ecosystems are inadequate, according to a recent National Research Council report. **Page 15**

New software product, NMRgraf, combines molecular modeling techniques with nuclear magnetic resonance spectroscopy data to create 3-D structural models of large molecules. **Page 16**

Books

"Superconductivity: The New Alchemy" by John Langone takes an upbeat look at the past, present, and future of superconductors. **Page 39**



Product Report

Increasingly stringent environmental regulations and tighter control over industrial wastewater drive demand for water treatment chemicals. **Page 17**

Chemical & Engineering News

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LETTERS

CHEMICAL SAFETY

Silane distillation explosion

SIR: We have, on two separate occasions, recently experienced explosions during the distillation of 1,2-dichlorotetramethyldisilane, a procedure that we have previously carried out numerous times without incident. In the first case, a distillation was inadvertently carried out in air atmosphere rather than under the usual conditions of a nitrogen purge. In the second example, a detonation occurred in a system that was supposedly under N₂ purge. Both explosions occurred at the liquid-gas interface in the glass distillation head and were accompanied by a fire that self-extinguished before proceeding down the column. The impact of the detonation was sufficient to shatter the apparatus, fortunately without injury.

Compounds containing strained Si-Si

bonds are known to undergo spontaneous air oxidation to the siloxane but in general chloro/methyl di- and polysilanes are reported to be "stable to air oxidation" [*J. Organomet. Chem.*, **94**, 367 (1975)]. We cannot be sure that the explosion was the result of oxidation as opposed to rapid hydrolysis of the silyl chloride (or some combination of both processes) but it has been our experience that hydrolysis of hot chlorosilanes, while extremely exothermic, does not result in explosion.

We recommend that anyone using this class of chloromethyldisilanes use adequate precaution when handling these compounds at elevated temperatures under atmospheric conditions.

Jonathan D. Rich

Manager, Silicone Materials Program
GE Corporate Research & Development

Flammable ammonia

SIR: Regarding Ernest J. Tews' letter (C&EN, Jan. 15, page 2), I too have been disturbed by the classification of ammonia as a nonflammable gas. Of course it is flammable.

One of the experiments I performed for firemen during my many years of teaching about hazardous chemicals was to feed ammonia gas and oxygen into an ordinary lab Meeker burner, adjust the gas flows, and ignite the flame with a propane torch. The bright yellow flame was proof enough.

Fred C. Trager
Barberton, Ohio

Chem Matters for high schools

SIR: I'm pleased to inform J. J. Jacobson (C&EN, Dec. 11, 1989, page 3) and any other readers who recall the periodical *Chemistry*, that the ACS Education Division initiated a new and eminently successful high school chemistry publication, *Chem Matters*, more than six years ago. With a current circulation of approximately 60,000 copies, this award-winning periodical supports the popularization and enrichment of chemistry for students through a variety of appealing and motivational articles, features, and activities.

I urge Jacobson and others not yet familiar with this excellent ACS initiative to become acquainted with *Chem Matters* and promote its extended use among schools and teachers in their areas. Sub-

scription information may be obtained from the Education Division, American Chemical Society, 1155—16th St., N.W., Washington, D.C. 20036, phone (202) 872-4590.

Henry Heikkinen

Chairman, Chem Matters Policy Board
Professor of Chemistry
University of Northern Colorado

Cover credit

SIR: It may be of interest to your readers that the instrument shown on the cover of C&EN, Feb. 26, is the Perkin-Elmer Cetus DNA Thermal Cycler. The person using it is Elena D. Katz, a senior researcher in our Biotechnology Product Department engaged in methods development for PCR technology.

Edward Bloch

Director, Corporate Relations
Perkin-Elmer Corp.
Norwalk, Conn.

Corrections

• Feb. 26, page 37: The University of Illinois' Chicago campus was misidentified as UI's Chicago Circle campus.

• March 12, page 19: The correct phone number for information on ordering EPA's report, "Methods To Manage and Control Plastic Wastes," is (800) 424-9346.

BIOMASS BURNING:

Environment hurt more than thought

Biomass burning—the burning of rain forests, savannah grasslands, agricultural wastes, and other biological materials—is far more widespread and dangerous to the environment than was previously thought, according to scientists attending the first international conference on biomass burning, held last week in Williamsburg, Va.

About 180 scientists and policy-makers from more than 25 countries attended the conference, which was sponsored by seven organizations, led by the American Geophysical Union and the National Aeronautics & Space Administration.

Biomass burning creates several greenhouse gases, as well as chemically active gases that cause acid rain and tropospheric ozone pollution. Researchers estimate that, in total, about 5% of Earth's surface is burned each year.

Just five years ago, the scientific community gave little attention to biomass burning, says conference

organizer Joel S. Levine, a senior research scientist at NASA's Langley Research Center. But recently, it has become the subject of intensive research.

Scientific estimates of the amount of biomass burned in the world each year are greater than they were a decade ago. Paul J. Crutzen, director of the atmospheric chemistry department at Max Planck Institute for Chemistry in Mainz, West Germany, says that some 3 billion to 5 billion metric tons of biomass carbon are burned annually, compared with 5 billion to 7 billion metric tons of fossil fuel carbon.

Meinrat O. Andreae, director of the biogeochemistry department at Max Planck Institute, calculates that the carbon dioxide from biomass burning is about 40% of that produced from all sources annually, and that the carbon dioxide from deforestation alone accounts for about 26%. Burning of the savannah in Africa is responsible for about one third of the global biomass burning.

Photographs taken by astronauts show that during the burning (dry) season, smoke areas in the Amazon have increased from scattered fires covering about 300,000 sq km in 1973 to continental-scale palls over about 3 million sq km in 1985 and 1988, reports Charles A. Wood, space scientist at NASA's Johnson Space Center in Houston. "You had better look at Earth in the near future if you want to see it, because soon you won't be able to see it," he warns.

Biomass burning has a number of important impacts. The nitrogen oxides, hydrocarbons, and carbon monoxide released in the combustion process lead to the formation of tropospheric ozone. Also, the nitric oxides and formic and acetic acids created during combustion cause acid rain. In addition, biomass burn-

ing, by altering soil nutrients, increases the emission of methane and various oxides of nitrogen from the soil for many months after the burn.

Biomass burning affects global climate in several ways, especially by creating vast amounts of the greenhouse gases carbon dioxide and methane. The changes in land surface resulting from biomass burning also alter climate. Because deforested land is not nearly so efficient as a tropical rain forest at returning rainfall to the atmosphere, burning vast stretches of rain forest reduces precipitation in the tropics.

As a result of the enormous quantities of biomass burned each year in the Amazon and in Africa, ozone levels there in the burning season are close to those in the industrialized world. Ozone concentrations in Africa are almost high enough to be toxic to plants, Andreae reports.

During the burning season, rain over virgin rain forests in central Africa and South America is as acidic as that which falls in Europe and North America. Jane Dignon, a researcher at Lawrence Livermore National Laboratory, California, attributes the high acidity in the tropics to biomass burning.

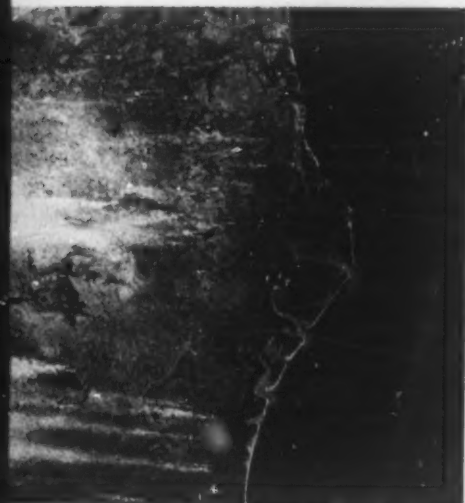
Information about almost every aspect of biomass burning is quite uncertain. Though experts generally agree that the amount of burning has accelerated greatly in the past few decades, the current global extent, the percentages of various ecosystems being burned, and the frequency of burn are known only roughly.

"We believe that more than 95% of global burning is human initiated and can be stopped once the world's leaders are aware of its detrimental environmental consequences," Levine says. "This is one area of science where we can effect a reversal

Biomass burning large source of global emissions

Million metric tons per year as C, N, or O	All combustion sources ^a	% from biomass
Carbon dioxide (gross)	8700	40 %
Carbon dioxide (net) ^b	7000	26
Carbon monoxide	1100	32
Methane	380	10
Nonmethane hydrocarbons	100	24
Ozone	1100	38
Ammonia	44	12
Nitrogen oxides (NO _x)	40	21
Nitrous oxide (N ₂ O)	13	6

^a Including fossil fuel and burning and all biomass burning. ^b Carbon dioxide released by all combustion minus that taken up by replacement vegetation. Sources: Meinrat O. Andreae, Max Planck Institute for Chemistry



Agricultural fires form white smoke plumes in infrared photo from space shuttle over East African coast

of a dangerous trend by raising awareness and public education."

Last Friday, conference scientists discussed global burning on a teleconference broadcast live on Public Broadcasting Service stations and by satellite around the world. Viewers questioned the panelists by using a toll-free phone number.

Bette Hileman

Plan for vital defense technologies issued

Efforts are moving on at least three fronts toward formulating a national technology policy. For example, a report released last week describes plans for developing 20 technologies rated by the Department of Defense as the "most critical to ensuring the long-term qualitative superiority of U.S. weapon systems."

Under a Congressional mandate, the White House Office of Science & Technology Policy is forming a National Critical Technologies Panel. This high-level panel will prepare by late fall the first of a series of biennial studies of up to 30 crucial defense and civilian technologies. Moreover, OSTP will soon issue a first, broad overview of technology policy.

Meanwhile, the Commerce Department is expected shortly to issue a report on critical technologies.

DOD's 272-page report is the second annual Critical Technologies Plan it has prepared (C&EN, April 3, 1989, page 24). Concerned that the U.S. is losing its technological edge, Congress has mandated in the past two defense authorization acts that DOD, in consultation with the Department of Energy, draw up such a plan and submit it by March 15 each year to the Senate and House armed services committees. The report will be the focus of a hearing this week before the Senate Armed Services Subcommittee on Defense Industry & Technology, chaired by Sen. Jeff Bingaman (D-N.M.), initiator of this and the OSTP mandate.

The 20 technologies include all four chemically related ones from last year's list, plus an addition. Two technologies—composite materials, and semiconductor materials and microelectronic circuits—rank in the highest of three priority groups, Group A. Three others—biotechnology materials and processes, high energy density (energy dense) materials, and superconductivity—are in Group C, which contains mainly emerging technologies. High energy density materials, which include improved rocket propellants and explosives, are new to the list.

For each technology, the report describes the reasons for its selection, current and projected manufacturing capabilities, development plans, related R&D in the public and private sectors, potential benefits for weapon systems and the U.S. industrial base, and current funding. DOD and DOE are spending \$3.1 billion on 19 of the technologies (funding of one is classified). Nuclear technologies are not included and will be addressed later separately.

The report also compares the U.S.'s competitive status versus other nations. As in 1989, Japan is "significantly ahead in some niches of technology" in five areas: semiconductor materials and microelectronic circuits, machine intelligence and robotics, photonics, superconductivity, and biotechnology materials and processes. The Soviet Union has a significant lead in some niches of just one technology, pulsed power. It is generally on a par with the U.S. in high energy density materials and two other areas.

The report is a "significant improvement over last year's," says Bingaman. It is the "most comprehensive effort thus far to sort out our defense technology priorities," and has substantial industry input. He hopes it will be "a building block" toward a national technology policy.

However, he adds, "it is still not a plan to get from here to where we want to be." Thus, DOD does not designate a lead agency for each technology, as Congress asked. "This is still more of a report on critical technologies than a plan for achieving specific goals by specific organizations in specific time frames with specific resources."

Richard Seltzer

New, powerful catalysts for methane conversion

Catalytic chemists at Oxford University in the U.K. have discovered a new series of ruthenium-based catalysts that provide very high activity and selectivity in converting methane to synthesis gas.

A research group, including Anthony K. Cheetham, of Oxford's chemical crystallography laboratory, has demonstrated that catalysts of the type $\text{Ln}_2\text{Ru}_2\text{O}_7$ (where Ln is a lanthanide) are extraordinarily active for the partial oxidation of methane to synthesis gas—for example, lowering the temperature required for the reaction from more than 1200 °C to only about 775 °C [*Nature*, 344, 319 (1990)]. These catalysts are ruthenium analogs of a number of rare-earth/tin oxides that have been used for the oxidative coupling of methane to ethylene.

Unlike most synthesis gas generating reactions, the partial oxidation reaction ($\text{CH}_4 + \frac{1}{2}\text{O}_2 \rightarrow \text{CO} + 2\text{H}_2$) is mildly exothermic and produces a synthesis gas with an unusually low H/CO ratio. This may be advantageous in future commercial operations by eliminating the need for a second-stage reactor to adjust the H/CO ratio, as is done today.

Cheetham's work is supported by the Gas Research Institute, Chicago, which has just renewed his funding for an extended period. According

Canada Could Get Three MTBE Plants

Canadian chemical companies are jumping into the octane booster, methyl *tert*-butyl ether (MTBE), in a big way. Right now, there are no MTBE plants in Canada. Soon there could be three.

The first to come on stream likely will be a 500,000 metric-ton-per-year unit to be built near Edmonton, Alberta, by a joint venture of Finland's Neste Oy and Petro-Canada.

Two other Canadian MTBE ventures are on the drawing board. Soquip, the Quebec provincial government's oil and gas holding company, may build a 500,000 metric-ton-per-year plant near Montreal, along with Italy's Ente Nazionale Idrocarburi (ENI) and Noverco (Montreal). And Nova Petrochemical could become the third Canadian MTBE producer with a 400,000 to 500,000 metric-ton-per-year plant the company is considering—possibly at Sarnia, Ontario, but neither site nor capacity has been set yet.

If all three of these plants are actually built, Canada's MTBE capacity could zoom from zero to about 1.5 million metric tons in a few years. And the Canadian MTBE producers should have little trouble marketing their output.

Demand for MTBE in the U.S. as an oxygenated fuel additive is soaring. There's little doubt that these Canadian companies have their eyes on the U.S. market. And exporting MTBE from Canada to the U.S. will become much easier after April 30. That's when, under the accelerated tariff cuts negotiated as part of the Canada-U.S. Free Trade Agreement, duties on MTBE will be eliminated. MTBE coming into the U.S. from Canada now has a tariff of 5.6% ad valorem.

Meanwhile, Canadian demand for MTBE also is likely to increase dramatically. Canada plans to eliminate lead additives in gasoline and has advanced the effective date of this move by two years, from December 1992 to December 1990.

For several years, Canada has been

MTBE capacity would be 1.5 million metric tons

Thousands of metric tons per year	Capacity
Petro-Canada, Edmonton, Alta.	500
Neste Oy	
Soquip, ENI, Noverco	Montreal, Que. 500
Nova Petrochemical	Sarnia, Ont. 500 ^a
TOTAL	1500

^a Possible capacity range is 400,000 to 500,000 metric tons.

reducing the level of lead allowed in gasoline. The present lead level allowable is 0.2 g per L. When lead is eliminated from use in all gasoline except that fuel used in critical farm, marine, and commercial vehicles, there will be a demand for octane in Canada that MTBE and other oxygenated fuels will likely be called upon to meet.

And last month, the Canadian government proposed regulations to reduce automotive emissions, which, if adopted, would take effect with the 1995 model year. The goal is to cut nitrogen oxide emissions 60% and hydrocarbon emissions 29%. To meet these standards, refiners no doubt would have to add MTBE, ethanol, or methanol to their gasoline.

In addition to potentially attractive markets, Canadian MTBE producers can depend upon a ready supply of raw materials. There are several methanol producers in Canada. And the country has an abundant supply of natural gas and crude oil from which to get butylenes.

Construction should start on the Neste Oy/Petro-Canada plant in Alberta next month and the unit could be on stream by the end of next year. Nameplate capacity is 500,000 metric tons per year but design capacity is 530,000 metric tons.

Already, the partners are looking ahead to expanding their MTBE plant beyond its 500,000 metric ton

capacity, if the MTBE market develops as expected. Methanol for the unit may come from Celanese Canada's nearby 900,000 metric-ton-per-year plant, but the company is still negotiating for methanol supplies, and other sources are available.

Nova Petrochemical has yet to make a go/no-go decision on its MTBE plant. "It's still under consideration and is of significant interest," says Keith McKee, who until recently was the company's general manager of business development.

In addition to the site and capacity, also still undecided is whether the company will build the MTBE plant alone or with another company. Nova had been considering a joint venture with Pequiven, the Venezuelan petrochemical company and Italy's ENI. "This is still an option," says McKee. No matter where the plant is built, the methanol feedstock would come from the company's own methanol plant at Medicine Hat, Alberta.

Most tenuous of the three Canadian MTBE projects right now is the one slated for Montreal. That's because the project depends upon whether a pipeline is built from Sarnia to Montreal to carry natural gas liquids to the Montreal area. The pipeline would be built by Interprovincial Pipe Line.

Spearheading the pipeline project is Soligaz, a consortium of companies that includes Quebec's Soquip, one of the companies involved in the proposed MTBE plant. The NGL pipeline already has been approved in principle by the federal government, but it must await final approval of the National Energy Board.

Interprovincial Pipe Line plans to seek final board approval this summer. If approved, construction could start early next year. Without the pipeline, the MTBE plant probably would not be built in Montreal because adequate feedstock would not be available.

Earl Anderson

PRODUCT REPORT

*Technicians sample and test
for contaminants
from aerated lagoon*



Water Treatment Chemicals: Tighter Rules Drive Demand

Ann M. Thayer
C&EN Northeast News Bureau

In the U.S., about 325 billion gal of water are used every day. Almost all of this water, used primarily by industry, municipalities (excluding residential and commercial), and power-generating utilities, must be treated. Physical, chemical, and biological methods are used for treating water to remove pollutants or contaminants that can interfere with its use, or to allow for its discharge into surface waters.

The overall market for water treatment chemicals totaled \$2.32 billion in 1988, according to a study

by Freedonia Group, a Cleveland-based research group. Nearly 12.9 billion lb of water treatment chemicals were sold that year. Because water treatment chemicals include both commodity and specialty-grade chemicals, the sizes of the major markets can differ widely when considered by dollar value or volume.

The industrial market, which covers a broad range of manufacturing, processing, and refining industries, accounted for close to a third of the total volume of chemicals used, but nearly 47% of the dollar value. Major industries, such as paper manufacturing, chemical processing, and refining, rely more heavily on

higher margin, lower volume specialty chemicals used as coagulants, dispersants, and corrosion inhibitors. In contrast, the municipal, utility, and institutional markets are dominated by the lower price, higher volume commodity chemicals such as chlorine, lime, caustic soda, and soda ash. These markets accounted for about 48%, or \$1.1 billion, of the value and about 53%, or about 7 billion lb, of the volume of materials sold. Similarly, the residential and commercial market used slightly more than 12% in volume, but spent only 5.5% of the total in 1988.

The markets for specialty chemicals are growing faster than those for commodity chemicals, explains William Weizer, vice president of the chemical and plastics division of Freedonia Group. The overall water treatment chemicals market is projected to expand 6.7% annually for the next few years, reaching \$3.2 billion by 1993. However, this represents only a 1.6% annual growth in volume. Industry use of specialty treatment chemicals will grow at a level 1.3% higher than that of the overall market. Chemical processing and refining industries will lead this growth at 9.5% per year through 1993. However, in the more mature municipal and institutional markets, growth will be nearly flat.

Chemical demand will be stimulated by increasingly stringent environmental regulations, says Weizer, and by tighter control over industrial wastewater.

The markets for water treatment chemicals can be broken down into five major applications—cooling, boiler, waste, supply, and process water. Cooling water, about 29% of the overall market, is the largest application for water treatment chemicals. The remaining four applications areas are nearly the same size.

In terms of real growth, the applications markets are growing slowly, says Peter Thomas, director

Federal laws limit chemicals in water

How water is regulated under federal law depends primarily on the its past and current usage. Under several laws relating to water, the Environmental Protection Agency oversees and directs state management of water quality standards. For example, pollutants entering surface waters are regulated under the Clean Water Act. The Safe Drinking Water Act protects drinking water sources and sets drinking water standards. Groundwater and hazardous wastewater are regulated under Superfund and the Resource Conservation and Recovery Act.

The Clean Water Act regulates contaminants discharged in municipal and industrial wastewaters. Under this act, which was amended and strengthened in 1987, EPA established technology-based limits on 68 pollutants from a list of 126 priority pollutants. These regulations were promulgated in response to a settlement in a 1976 suit brought by the Natural Resources Defense Council. Based on the best available technologies economically achievable and on the best practicable control technologies currently available, these limits are known as the organic

chemicals, plastics, and synthetic fibers guidelines. They were challenged in court by members of affected industries, but were upheld in a March 1989 decision.

Effluent guidelines under the Clean Water Act are used by states to issue National Pollutant Discharge Elimination System permits. These permits specify the amounts of different pollutants that may be directly discharged, and they set up monitoring and reporting schedules. Pretreatment standards for industrial discharges into municipal treatment plants, as well as minimum treatment standards for municipalities, are also part of the Clean Water Act's guidelines.

The impact of the organic chemicals, plastics, and synthetic fibers guidelines and the 1987 Clean Water Act amendments have yet to be felt. Issues raised in the amendments are just now beginning to be addressed by EPA. These include regulations on nonpoint source pollution and a permitting program for storm water discharges by industry and municipalities, regulations on the management and disposal of residual sludges from wa-

ter treatment processes, and further enforcement of compliance with effluent toxicity regulations.

On the water supply side, the Safe Drinking Water Act directs monitoring and treatment of drinking water and aims to minimize contamination of surface- and groundwaters. It focuses on the presence of lead, radionuclides, and microbiological contaminants, as well as on organic and inorganic chemicals. Monitoring for currently unregulated organics and inorganics is also directed.

Amendments to this act in 1986 directed EPA to establish maximum contaminant levels and best available technologies on 83 pollutants by June 1989. States are required to adopt regulations at least as strict as the standards outlined by EPA. To date, about 15 final maximum contaminant levels have been established, about another 40 have been proposed, and 25 more are expected this year. The regulations become effective 18 months after promulgation, and final limits for all 83 contaminants are not expected until 1992. In 1991, EPA is also expected to propose rules for disinfectants and their by-products, such as chlorinated organics.

of marketing at Drew Industrial, a division of Ashland Chemical. The market for boiler water treatments is estimated to grow at less than 2%, whereas cooling water uses will grow 2 to 4%. High capacity utilization helps to keep water treatment chemical markets stable, but decreases in manufacturing and production—which can occur in a slower economy or a recession—can hurt growth for the industry. The market for wastewater treatment will see the most real growth, at 5 to 7%, says Thomas, with activity attributed primarily to environmental concerns.

Treatments for most uses of water consist of proprietary specialty formulations supplied by water treatment companies. The industry is dominated by six firms—Betz Laboratories, Calgon, Dearborn, Dexter (Mogul), Drew Industrial, and Nalco Chemical. To varying extents and strengths, each firm services all the major markets. The smaller Olin

Water Services and Hercules Water Management businesses have been acquired in the past few years by Drew and Calgon, respectively. Chemed's Dubois Chemicals business has about \$25 million in sales in the water treatment area. The wide variety of commodity and specialty chemicals used in formulations are supplied by numerous chemical manufacturers serving other industries in addition to water treatment.

In addition to selling chemical formulations, water treatment companies charge for services associated with the application of their products and often for the lease of equipment. "The water treatment industry is an operating expense dominated market," explains Thomas M. Laronge, a technical consultant based in Vancouver, Wash. Customers tend to be interested only in how much it costs on a daily basis to have their water treatment needs for uninterrupted and efficient plant

operations addressed. Thus, the services provided are often used as a means for differentiating what are otherwise similar chemicals, comments Laronge. "Water treatment is really a process, rather than a product, that occurs between the end user and the water treatment company."

This process includes analyzing a plant's water, developing a material balance for a desired application, and determining the appropriate treatment to minimize the effects of contaminants or naturally occurring impurities in water. It also can include implementing, monitoring, and upgrading the water treatment process, and providing analytical laboratory services for customers. When problems arise, explains Laronge, they're usually the result of a breakdown in the overall treatment process rather than in product quality.

To compete in what is a generally mature market for chemicals, the

Product Report

major companies stress the importance of their added services, technological advances in product design and application, and product quality. The "value-added services" have contributed to the profitability of specialty formulations that are sold as part of water treatment programs. They include the design of water treatments, computer-based process monitoring and maintenance, emergency response services, regulatory and environmental consulting, and even the disposal of shipping containers for the chemicals.

"As a result of trying to meet quality control demands, the trend in some industries is to enter sole-supplier relationships," says a spokesman for Betz Laboratories in Trevose, Pa. For the large companies, which may patent their products, providing services is another means to compete with "over-the-counter" competition from those who attempt to copy and supply formulations. Betz and Nalco Chemical, of Naperville, Ill., are the two largest water treatment companies. Betz had 1989 sales of \$249 million for its heavy-industry water treatment divisions, and Nalco had 1989 sales over \$270 million for its water and waste treatment division.

Calgon, based in Pittsburgh, ranks itself about third in the industry, but as a subsidiary of Merck & Co., it does not report separate sales figures for its business. Drew, based in Boonton, N.J., and Dearborn (a division of W. R. Grace & Co.), based in Lake Zurich, Ill., fall somewhere in the middle range of the six largest companies. Although Grace reported 1988 sales in water treatment of \$183 million, its figure includes other water treatment operations. Dexter Water Management Systems, a division of Dexter Corp. located in Chagrin Falls, Ohio, had sales estimated well below \$100 million in 1989.

"One of the aspects of our business that has really taken off in the past several years is the control aspect," says Bruce Grotefend, director of marketing for Calgon. Control systems are produced under various tradenames by all the major companies. The goal is to automate the water treatment process by com-

puter monitoring, chemical feed control, and data management.

Adds Ed James, director of cooling product management at Betz Industrial: "It's an emphasis and a commitment to bring the control of water systems up to the level of the control that companies have on their processes." Such systems allow for steady-state operation of chemical or refining processes and include correcting for changes in pH brought about by accidental overfeeds of acids, treating for changes in contaminants from various processes, and adjusting loads when other processes or equipment are brought on-line. This can result in efficient use of equipment, decreased maintenance, energy savings, and limited production shutdowns. Monitoring systems also alert the water treatment company to emergencies.

Another service offered, in response to customer concerns about the handling and disposal of drums, is alternative delivery methods for chemicals. "Nalco is working to get out of the drum business," says Mary Kay Kaufmann, marketing manager of Nalco's basic industry group. Semibulk containers of about 300 gal are becoming widely used by the industry to deliver and store chemicals. The water treatment companies collect, clean, and refill these semibulk containers. Capital costs for the containers, as well as costs for the extra handling, disposal of any hazardous chemicals after cleaning, and refilling the containers, have become part of the water treatment chemical supplier's business and may be passed on to customers.

By far the most important service, according to the water treatment companies, is that of being consultants to customers who want assurance that the chemicals are applied properly. In this role, many companies may require that only their chemical treatments be used with equipment leased to customers. Still, underlying all the service aspects is the basic question of how well the water treatment process works.

Water treatment is chemically complex, containing many variables related to local water conditions and characteristics—namely, the amounts and types of impuri-

ties and contaminants present. Stable mixtures of a few to a dozen chemicals, in which each chemical performs properly under conditions of pH, temperature, and water composition and purity, must be developed. R&D plays a significant role in the water treatment industry's efforts to produce new products and optimize formulations. Nalco and Betz spend an estimated 4% of sales, or about \$10 million, on R&D. Formulations are sometimes custom blended to take into account local conditions, water quality, how the water is used, and the design and construction of the plant equipment.

"In the specialty chemical market," says Kaufmann, "the challenge is to develop new innovations in [chemical treatment] technology." Yet, in any one of the larger applications for water, the types of problems to be addressed are fairly consistent. For example, in cooling and boiler water treatments, the concerns center on corrosion and scale inhibition. Corrosion, an oxidation-reduction reaction in which a metal surface is converted to its oxide, is caused by the presence of dissolved oxygen and is affected by the presence of suspended solids, temperature, pH, hardness, and ion concentration. Scaling is caused by the deposition of insoluble salts on heat transfer surfaces. A third concern, preventing biological growth, can be added to the list for cooling water treatment. Together, these



Pilot plant cooling tower system is used as model in R&D

Product Report

problems result in heat transfer losses and decreased efficiency, metal degradation and pipeline failure, and blockages and flow problems.

Concern is focusing on some of the water treatment chemicals used in industrial cooling and boiler water treatments because of the potential for being discharged in wastewater. "The environmental atmosphere, with stricter regulations, is changing the business for both producers and users of water treatment chemicals," says Thomas of Drew. "It's more costly to meet newer federal [Environmental Protection Agency] requirements." For the water treatment companies, this means more testing, more data collection, and supplying more information on the chemicals used in the products.

Meeting new regulations and stricter limitations on chemical contaminants in water can be achieved at a cost, explains Thomas, "but that cost is likely to be high." And, although tighter rules make doing business more expensive and complicated, they do signal growth for the industry, which is expected to expand—not only with more treatment required, but with new technologies and products developed to treat previously unregulated contaminants.

For users of water treatment chemicals, environmental concerns mean complying with federal guidelines on discharges of waste chemicals from industrial processes. To address concerns from both ends, water treatment firms are providing environmental counseling services. These services are aimed at keeping customers aware of regulations that pertain to their discharge permits, helping them come into compliance with new effluent guidelines, and addressing concerns about the treatment chemicals themselves.

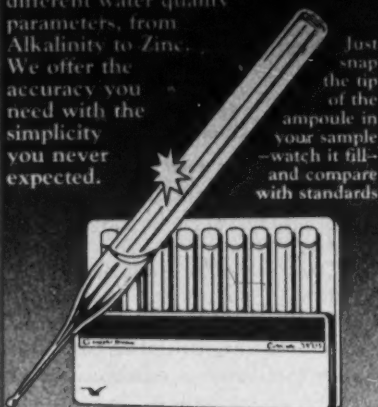
"[Addressing concerns] can require us to change a program to one that is more environmentally acceptable," says Tom Schmucker, director of boiler product management at Betz Industrial. Biocides, used to prevent algal, fungal, and bacterial contamination in cooling water systems, are an example. Like pesticides, all biocides are registered under the Federal Insecticide, Fungicide & Rodenticide Act and come under

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pH adjusters/softeners are largest volume chemicals

Millions of lb	Paper Industry	Chemical/ refining	Other Industry ^a	Municipal/ utilities	Residential/ commercial	Total
Coagulants/flocculants	856	172	234	628	4	1,894
Filter media/adsorbents ^b	11	28	56	148	18	261
Oxidizers/disinfectants ^c	227	114	179	1444	222	2,186
pH adjusters/softeners	680	209	1008	4369	0	6,266
Corrosion inhibitors	81	129	184	9	0	403
Sodium chloride	0	67	82	0	1342	1,491
Other	20	21	35	286	0	362
TOTAL	1875	740	1778	6884	1586	12,863
TOTAL (\$ millions)	\$396	\$267	\$427	\$1106	\$128	

Note: 1988 U.S. markets. a Includes textile, food and beverages, paints and coatings, electronics, rubber and plastics, metals, mining, and oil and gas. b Physical filtering methods not included. c Synthetic organic biocides not included. Source: Freedonia Group

close environmental scrutiny when discharged as part of cooling water. If an effective replacement cannot be found, the goal is to then look for materials that can be neutralized or detoxified by a subsequent treatment.

Biocidal treatments can be oxidizing or nonoxidizing chemicals and include chlorine, chlorine dioxide, bromine and bromine com-

pounds, sodium or calcium hypochlorite, isothiazoline, organochlorine or organobromine compounds, and quaternary ammonium salts. Their effectiveness depends upon the type of biological growth, pH sensitivity, and presence of other contaminants. Concentrations used range from less than 0.1 mg per L to as much as a few tens of milligrams per L of water treated.

Bromine hydantoins and quaternary ammonium compounds are receiving attention as replacements for chlorine, says Doug Murray, business manager for water treatment chemicals at Lonza. The problems in handling pressurized gas, as well as concerns about the formation of toxic chlorinated organics in waste streams, are contributing to the move away from chlorine. For disinfection, chlorine gas has long been one of the least expensive alternatives.

Hydrazine, a suspected carcinogen, used as an oxygen scavenger and metal passivator to prevent corrosion in boiler and steam systems, is another water treatment chemical about which there is concern. Dearborn has patented the use of diethylhydroxylamine as a replacement for hydrazine. Cyclohexylamines and sulfites are also used as oxygen scavengers in corrosion control. Some of the neutralizing amines, notes Schmucker, are now generating concern.

Most attention in the industry has focused on chromates once used extensively for corrosion inhibition in cooling water equipment. Chromates protect metal alloys from corrosion by producing a protective metal oxide film on the metal surface. Concern about the presence of chromium is directed at airborne heavy metals from misting off open cooling towers and in wastewater discharges. Chromates were banned in January for use in comfort cooling (air-conditioning) uses, and limitations on other uses are generally expected.

"To some degree [the ban] has been anticipated," explains James of Betz, "and is not a problem because we already have nonchromate programs in place." Replacement products are based on inorganic phosphates and polyphosphates, or all-organic treatments, used in various mixtures with zinc, phosphonates, and dispersants. Economic considerations and the type of cooling system employed (recirculating or once through) will determine which treatment method is most cost-effective.

Only about 10% of all U.S. plant locations continue to use chromates. However, the refining industry still

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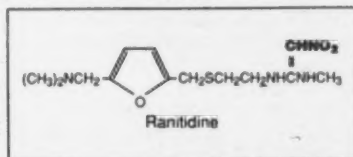
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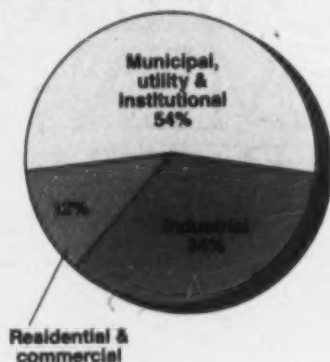
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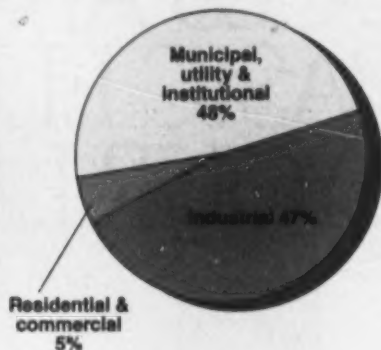
Municipal uses dominate chemicals consumption ...



1988 total = 12.9 billion lb

Source: Freedonia Group

... but industry spending is nearly as much



1988 total = \$2.3 billion

relies heavily on their use. "It's a common misconception that chromates are still desired and necessary," says James. "They are really a very low percentage of our sales." The overall market for corrosion inhibitors was 403 million lb in 1988, or \$395 million, primarily for use in industrial, rather than municipal or residential, applications. Growth is expected to be 9% per year for corrosion inhibitors with the more expensive replacements and the eventual changeover of the refining industry to nonchromate programs contributing to this growth.

Chromate programs tend to be more forgiving than nonchromate programs when errors occur, explains Kaufmann of Nalco. Chromates operate best in a pH range of 6 to 7, which is a more corrosive environment, but one in which there is less likelihood of the formation of scale. However, nonchromate programs operate at higher pH and, if not properly controlled, scale can form rapidly and detrimentally affect heat transfer. Under the older chromate programs, the consequences were slower, longer term corrosion, rather than scale, and less immediate effects on heat transfer and operation. "As a result," she adds, "automated control and feed [of the treatment chemicals] is becoming much more emphasized."

Hand in hand with the change to nonchromate programs have been improvements in scale control agents. Common scales include

magnesium hydroxide and calcium carbonate, calcium sulfate, and calcium phosphate, formed from the presence of magnesium and calcium "hardness" ions. Calcium carbonate scale formation can be inhibited by polymeric inorganic phosphates, generally the sodium and potassium salts. These include salts of pyrophosphate, triphosphate, and hexametaphosphate, which can suppress crystal formation on the metal surface. Organic phosphates and phosphonates may also be used. Organic polymers including polyacrylate, polyacrylamides, polymethacrylate, polymaleates, and their copolymers are being introduced as effective scale control agents. At low molecular weights, 1000 to 10,000 atomic mass units, and in milligrams-per-liter quantities, the polymers inhibit crystal growth and act as dispersants that inhibit precipitation. Suspended solids or nonadherent scale sludges can be removed with the water.

The increased concentration of phosphates to prevent corrosion can result in the formation of greater amounts of calcium phosphate deposits. According to Calgon, new inhibitors such as acrylic acid-hydroxypropylacrylate copolymer, styrene sulfonic acid-maleic acid copolymer, acrylic acid-sulfonic acid copolymer, and phosphino/acrylic acid-organosulfonic acid copolymer have been developed. Other possible dispersants are lignin- or cellulose-based and are more easily de-

graded than synthetic polymers in wastewater, but must be used in higher concentrations and can contribute to foaming.

Defoamers account for 76 million lb, or about 4%, of the water treatment chemicals market. Dispersants, surfactants, and emulsifiers are also used to suspend solids, corrosion by-products, biological matter, and dirt. Deemulsifiers are used to break up oils and greases that would otherwise foul heat exchange systems. Market figures for dispersants are included in the overall category of coagulants and flocculants.

Depending on the characteristics of influent water for industrial uses, particularly in boiler water use where evaporation causes the concentration of impurities, the water may require pretreatment to remove solids, minerals, and impurities. A clarification step may involve pH adjustment and treatment with coagulants and flocculants to remove dissolved solids and some mineral salts. These treatments are closely related to those used in wastewater treatment. Other pretreatments may include demineralization by ion-exchange or ultrafiltration methods.

Ultrafiltration methods are generally based on membrane separation technologies about which few technical details are publicly available. In reverse osmosis, semipermeable membranes are used to separate pure water from water containing salts or other materials such as organics or solids. Purified water flows through the membrane, rejecting dissolved materials when an external pressure is applied to reverse the osmotic process.

Cellulose acetate and polyamide are some of the more common materials used in what are complicated, multilayer membrane systems. Dow, Du Pont, and Allied-Signal are major producers of membrane systems used largely in the desalination of brackish water as a source for drinking water. Advances in membrane technology, including more effective ones that are resistant to microbiological contamination, are expanding large-scale water treatment applications. But the cost of installation and operation can be prohibitive.

Ion-exchange resins, in columns

or beds, are used extensively to soften water by swapping ions bound to the resin with those present in the water. For example, in water softening with a cation-exchange resin, magnesium and calcium ions are replaced with sodium. Resins can be anionic or cationic. When used for complete demineralization of water, both positively and negatively charged ions are removed and exchanged with hydrogen and hydroxyl ions in a stepwise or mixed resin process. Since organics and solids will foul the resins, ion exchange generally follows other treatments.

Ion-exchange resins are predominantly styrene-based polymers and copolymers with divinylbenzene. Phenolic- and acrylic-based resins are also used. Acrylic resins are an important part of Rohm & Haas' ion-exchange resin business, adds Jack Gallagher, the company's North American regional director and worldwide codirector for ion-exchange resins. Rohm & Haas and Dow are two of the leading manufacturers of ion-exchange resins. The market for ion-exchange resins reached 126 million lb valued at \$209 million in 1988. The resins are generally sold through water treatment companies or distributors for installation in new equipment or replacement in existing equipment. Water treatment companies often service ion-exchange systems, and treatment acids or bases will regenerate the resins for repeated use.

Although easy to control and resulting in high-purity water, particularly for chemical process or

Cooling water uses lead treatment chemicals market



1987 total = \$2 billion

Source: Kline & Co.

power-generating uses, ion exchange is a relatively expensive treatment method. Resin costs average more than \$1.50 per lb, and, although they can be regenerated and reused, there are also capital costs for equipment. Operating costs, including replacing fouled or degraded resins, and downtime for regenerating or replacing resin beds are among the financial considerations.

Ion-exchange resins are used extensively in the municipal and institutional markets for water softening and other drinking water purification applications. The water treatment market is a very mature market, comments Gallagher. Specialty applications for removing heavy metals, producing ultrapure water for electronics applications, removing radionuclides in nuclear power plants, and for separation processes in chemical processing are the growing markets and will re-

quire resins with unique performance characteristics. Ion-exchange resins are also finding more use in treating water for nitrite, nitrate, and some organic contaminants.

Although regulatory pressures may cause a rise in the application of specialized treatment techniques to remove small amounts of specific contaminants, industrial and municipal wastewater treatment, historically, has focused on simple solids removal, pH adjustment, and disinfection.

Wastewater treatment consists of three major stages. Primary treatment is the removal of solids and biological oxygen-demanding substances by settling, filtering, or screening the water. Secondary treatment most often involves biological treatment. This includes activated sludge or attached growth treatments in which naturally occurring aerobic microbiological organisms digest contaminants in the water. Tertiary, or advanced, treatment may follow to remove low levels of organic or inorganic toxic contaminants.

Wastewater from industrial sources can contain more unusual chemicals, such as metals and organics, or more concentrated or toxic pollutants than municipal sources. Most industrial wastewater is treated on site in plant treatment facilities and directly discharged under National Pollutant Discharge Elimination System permits and must be treated to meet effluent standards. Wastewater that is discharged by a plant into a municipal treatment facility must be pretreated to meet certain standards set by the municipality based on its ability to handle certain contaminants. The permitted limits—based on EPA organic chemicals, plastics, and synthetic fibers effluent guidelines under the Clean Water Act—are set and enforced on the state and local levels. State water quality standards tend to be more stringent than EPA guidelines.

Along with industrial cooling and boiler water applications, polymers are finding extensive use in wastewater treatment to remove suspended materials. In primary or secondary clarification steps, and in later sludge-dewatering steps, polymers are replacing more traditional co-



In new water treatment process, UV light activates hydrogen peroxide

Demand for water treatment chemicals to grow

Millions of lb/\$ millions	1988		1993		2000		% annual growth	
							Volume	Value
Coagulants/flocculants	1,894	\$ 363	1,985	\$ 500	2,085	\$ 765	1.5%	6.4%
Filter media/adsorbents	261	320	315	470	400	770	0.8	7.6
Oxidizers/disinfectants	2,186	733	2,380	945	2,675	1280	3.6	4.8
pH adjusters/softeners	6,266	256	6,780	330	7,425	450	1.7	4.8
Corrosion inhibitors	403	395	515	645	715	1110	1.4	9.0
Defoamers	76	95	90	125	110	175	4.9	5.2
Fluorides	286	128	300	160	320	205	3.1	4.0
Sodium chloride	1,491	34	1,585	40	1,690	45	0.9	2.4
TOTAL	12,863	\$2324	13,950	\$3215	15,420	\$4800	2.7%	6.2%

Source: Freedonia Group

Water treatment chemicals fall into several general classes based on their properties and function. Whether for industrial processes, municipal uses, or waste removal, water treatments are generally mixtures of different inorganic and organic chemicals, both commodity and specialty, designed to address specific needs.

Coagulants and flocculants: These materials neutralize charged colloidal and suspended materials, allowing them to agglomerate. They include inorganic chemicals such as aluminum sulfate (alum), ferric chloride, ferric sulfate, sodium aluminate, and lime (CaO). High molecular weight organic polyelectrolytes can be designed to function as coagulants, whereas lower molecular weight polymers function as dispersants to prevent scale formation or fouling. Such polymers are generally based on polyacrylamide, often copo-

lymerized with monomers containing charged groups, polyamines, or polyacrylates.

Filter media and adsorbents: Activated carbon and ion-exchange resins account for the largest portion of adsorbent media in water treatment. Ion-exchange resins, used to demineralize water, often consist of cationic or anionic polystyrene-based copolymers. Granular activated carbon is used in columns or beds to remove water-soluble organics.

Oxidizers and disinfectants: Used to remove biological contamination, odors, and taste from water, these chemicals cover a wide range of organic and inorganic treatments. Chlorine gas and chlorine derivatives (chlorine dioxide, sodium and calcium hypochlorites) are commonly used. Bromine and bromine compounds are gaining in use as pos-

sible replacements to chlorine-donating inorganics and organics. Other oxidizing treatments include potassium permanganate, hydrogen peroxide, and ozone.

pH adjusters and softeners: Caustic soda, soda ash, lime, acids, and bases are used to change the acidity or alkalinity of water. Combined with coagulants and flocculants, they can be used to form insoluble salts, which can be removed by precipitation. Water softening involves the formation and precipitation of insoluble calcium and magnesium salts to remove the metal "hardness" ions that form scale on surfaces exposed to water.

Corrosion inhibitors: Corrosion, an oxidation-reduction reaction in the presence of dissolved oxygen, is a major cause of metal degradation in water systems. The process can be inhibited through the formation of protective layers on the metal. Chromate salts, inorganic and organic phosphates and polyphosphates, or all-organic treatments are common corrosion inhibitors.

Defoamers: Used primarily in industrial applications, such as pulp and paper manufacturing, defoamers include oil-based antifoam agents.

Fluorides and sodium chloride: These materials are used almost entirely in the municipal and residential markets for water fluoridation and water softening uses, respectively.

agulants and flocculants such as aluminum sulfate (alum), ferric chloride, ferric sulfate, sodium aluminate, and lime. Still, the inorganic commodity chemicals dominated the market for coagulants and flocculants in 1988. Alum accounted for 59%, or 1.1 billion lb, but only 31% of the market value. Alum is used to a very large extent in raw water treatment, municipal wastewater treatment, and water treatment in paper manufacturing. In contrast, at more than 13 times the price per pound, organic treatments accounted for only 8% by weight, but 55% in dollar sales. Iron salts and other inorganics make up the remaining market.

When used, alum forms a gelatinous floc of aluminum hydroxide

that adsorbs and settles out suspended and colloidal matter. Positively charged inorganic coagulants neutralize negatively charged colloidal species and cause them to agglomerate. Other inorganic chemical treatments, including lime and caustic soda, precipitate out metal hydroxides or form insoluble inorganic salts such as calcium carbonate or calcium sulfate. Added coagulants can help to increase the speed of settling of the precipitated material. Because of the quantity needed, the inorganic treatment chemicals themselves contribute greatly to the volume of sludge produced by flocculation. Polymers, although more sensitive to aqueous conditions, are used in much smaller quantities and produce sludges with

a higher percentage of solids to trapped water.

The water-soluble polymers are all high molecular weight polyelectrolytes, on the order of 10^5 to 10^7 amu, such as polyacrylamides, polyamines, polyacrylates, and their copolymers. The polymer's behavior is determined by a combination of chemical structure and molecular weight. Through copolymerization with different functional monomers, the ionic character of the materials as anionic, cationic, or neutral species can be determined. For example, in polyacrylamide polymers, the amide groups are hydrolyzed to form carboxylate groups, the anionic nature determined by the degree of ionization. Copolymerization with maleic anhydride, methacrylic

acid, and acrylic acid can introduce carboxyl groups.

There are many manufacturers of specialty water-soluble polymers. They include most of the water treatment companies or their parent companies, and others, such as American Cyanamid, Rohm & Haas, and Dow, which have well-established positions in the water treatment polymer market. National Starch & Chemical Co. is the sole manufacturer of sulfonated polymers, primarily polystyrene sulfonate, for water treatment. Polymers are often blended with inorganic coagulants and flocculants in formulations. The complementary behavior of these materials as mixtures is sometimes not well understood, or remains a carefully guarded trade secret. Such mixtures can minimize the amount of metal hydroxides that would be formed with inorganic coagulants while offsetting some of the polymers' sensitivity to water conditions.

Cationic polymers also find some application but can be somewhat

more expensive to produce. These can be acrylamide-based with a cationic monomer, or polyamines. Other cationic polymers are homopolymers of epichlorohydrin-dimethylamine or dimethyldiallylammonium chloride, or copolymers with acrylamide.

Two chemicals specifically labeled as water treatment chemicals and regulated under the Safe Drinking Water Act are acrylamide and epichlorohydrin. Eric W. Muchmore, business manager for water treatment chemicals in American Cyanamid's specialty polymers department, explains that either chemical could appear in water treatment polymer formulations if there is unreacted monomer from the production process. With careful control in manufacturing, EPA limits on residual acrylamide and epichlorohydrin can be met and maintained by monitoring product quality.

In a competitive and growing market, manufacturers of the specialty polymers hesitate to reveal

the actual composition of their copolymers. Water treatment polymers are carefully designed to separate out finer particles, add weight to the floc, and stabilize the resulting sludge by keeping solids together. Different types of solids, resulting from chemical or paper manufacturing processes, require different polymer treatments. Biological sludges are particularly difficult to treat, notes Muchmore.

Product performance—the ability to produce sludges with lower water content and a higher percentage of solids—is very important. When initially formed, sludge from wastewater may be only a few percent solids, increased to around 20% after being dewatered. The mechanical properties of the sludge depend on the polymer used and affect how well the sludge can be dewatered on equipment such as belt filters and presses. "The polymer supplier who can show higher [sludge] cake solids," says Muchmore, "is the one who is going to win bids."

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"Every percent [of] water that is removed has significant impact," he says. "Millions of dollars in disposal and operating costs can be saved from a few percent change." The rising cost of transporting and disposing of sludges has become a major concern for both industry and municipalities. In the past, about 25% of sludge has been incinerated, explains Muchmore, and about 75% placed in landfills. Tighter regulations are being imposed on the water content and composition of sludges that can be disposed of in landfills. A ban on ocean dumping of sludges will also go into effect this year.

Many see incineration, which also requires sludges with a higher solids content for more efficient burning, as a viable option. The obstacles to incineration include restrictions on materials that can be burned and opposition to the construction and use of incinerators for waste treatment. Sludges containing hazardous wastes are regulated under the Resource Conservation & Recovery Act. Further regulations on sludge management and disposal will result from the 1987 amendments to the Clean Water Act.

Those amendments, guidelines on organic chemicals, plastics, and synthetic fibers, and the Safe Drinking Water Act regulations are changing how industry and municipalities will have to treat water and wastewater in the near future. Traditionally, wastewater treatment, particularly municipal, is a process to neutralize the water, separate solids, remove organics with biological treatment, disinfect, and control odors. Most of this treatment requires only a few commodity chemicals—alum, lime, caustic soda or soda ash, and chlorine. Commodity chemicals such as caustic soda, soda ash, and acids used for pH adjustment accounted for nearly 1.4 billion lb or about 11% of the total water treatment chemical volume in 1988, whereas 4.9 billion lb of lime were used. Chlorine and chlorine derivatives made up 85%, or 2.1 billion lb, of the market for disinfectants and oxidants in 1988.

When commodity chemicals alone are needed, they may be purchased directly from suppliers, rather than

through water treatment companies. The water treatment companies will have increasing involvement in wastewater treatment as new technologies are needed to meet tighter regulations. A new market area targeted by Nalco is in providing consulting and product services on the biological treatment of wastewater. The needs in this area are twofold, explains Kaufmann. An optimum environment must be created for the microorganisms to grow and digest wastes and the desired organisms must be present to digest specific contaminants. This can involve "troubleshooting" to bring an activated sludge or aeration lagoon back into line and providing "formulations" of isolated, naturally occurring biological organisms. "If you can find a microorganism that will remove a particular organic, you can pretreat the waste stream before it hits the treatment facility and overloads the plant," says Kaufmann.

Stricter effluent guidelines under the Clean Water Act and drinking water standards under the Safe Drinking Water Act are setting limits between 1 mg per L and 50 ng per L on more than 100 organics, pesticides, and inorganics. On average, limits are now reaching well into the parts per billion, and even parts per trillion, range. In some cases, the technologies may not yet exist, or can be prohibitively expensive, to treat for certain materials or to reach the low levels proposed. Such methods are generally termed tertiary or advanced treatments.

One advanced treatment for the removal of organics is adsorption onto another medium. Although biological treatment can remove about 95% of suspended solids and of the biological oxygen demand, effluent levels of some organics may need to be lower. Activated carbon is considered the best available and most cost-effective technology under the Safe Drinking Water Act to adsorb organics in producing potable water. It can be used as a pretreatment to remove organics that may be toxic to microorganisms, or in combination with or following biological treatment to reach very low effluent levels. In industrial applications,



Computers are used to monitor and control water treatment

it may be used for the removal of hazardous compounds, to improve water quality for reuse, or to meet pretreatment or discharge standards.

In 1988, \$111 million worth, or 135 million lb, of activated carbon was used in water treatment. Activated carbon comes in two forms, granular and powdered, produced mainly by Calgon Carbon, American Norit, and Westvaco. Granular activated carbon is used in beds and columns whereas powdered carbon may be mixed with the water, then separated out by settling or filtration.

In the late 1970s, activated carbon producers expanded capacity in anticipation of regulatory measures for drinking water. However, the regulations were not enforced and a period of overcapacity resulted. "We believe now that the Safe Drinking Water Act amendments provide clear direction for where we are heading," says Roger Zanitsch, vice president, marketing and sales for Calgon Carbon. "One of the big growth areas of the 1990s will be water treatment." Final regulations on drinking water and groundwater, where activated carbon is used to strip organics, may affect activated carbon consumption.

"Any time specific organic chemicals in water are identified," he adds, "it favors the activated carbon technology." Activated carbon adsorbs most organics, but favors higher molecular weight compounds.

The carbon can be regenerated by thermally or chemically removing adsorbed materials. Calgon reprocesses activated carbon for its customers and sells directly to users and to contractors building water treatment facilities. The company also supplies the systems it builds for groundwater treatment.

The scale of the application will determine whether it is economically feasible to reprocess or replace the carbon. Typically, about 10% of the material is lost due to attrition and reprocessing, explains Zanitsch. In taste and odor control applications with low dose rates, it is cost-effective to replace the carbon every three to four years. Because of the low rate of adsorption for low molecular weight organics, other removal methods may be more cost-effective.

Thus activated carbon is not an effective method to remove trihalomethanes (THMs), such as chloroform, bromoform, bromodichloromethane, and dibromochlorometh-

ane. Final EPA regulations on THMs, suspected carcinogens formed by the chlorination of organics in water, are expected in the near future. Activated carbon is suggested as a way to remove their organic precursors.

Another approach to decrease THM concentrations is to relocate the point of chlorine addition in conventional processes to where the organic content is lower. After disinfecting with chlorine, water can be dechlorinated, to avoid reaction with naturally occurring organics, by dosing with sulfur dioxide as a reducing agent. Alternative disinfectants for drinking water are gaining attention as a means to prevent the formation of THMs and thereby avoid expensive treatment methods.

Possible replacement oxidizing chemicals include ozone, chlorine dioxide, organic halogen (Br and Cl) donors, sodium or calcium hypochlorite, and potassium permanganate. Each of the chemicals varies in effectiveness against contami-

nants, and consideration must be given with regard to handling, and to environmental and health issues. Although not forming trihalomethanes, other chlorinated organics may be formed with some chlorine derivatives. Despite being considerably more expensive than chlorine, many alternative disinfectants are expected to increase in use.

Hydrogen peroxide use is seeing growth as a replacement for chlorine in odor control, for removal of hydrogen sulfide and other sulfur compounds, and as a means to detoxify or destroy organic chemicals. In 1988, 62 million lb of hydrogen peroxide were used in water treatment, with municipal and institutional use accounting for 69% of use. The largest producers are FMC, Interlox, Du Pont, and Degussa.

"For environmental applications—water, wastewater, and hazardous waste treatment—compounded annual growth rates are expected to exceed 10% per year through 1995," says Robert S. Kouk, development

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manager for the environment at Interlox. Municipalities are a fairly mature market, where treatment consists of simple dosing with hydrogen peroxide to reduce odor. Hydrogen peroxide is generally sold as a raw material to users and may not require large capital or operating costs to implement its use.

Despite its reputation, producers indicate that it is stable, can be handled safely, and is reasonably cost-effective in light of advantages it may offer over other treatments. For example, in comparison to other treatment technologies that isolate, precipitate, or transfer the pollutant to an adsorbant, hydrogen peroxide can eliminate a pollutant completely with no residuals for disposal or reduce it to degradable levels. "Environmentally, it's one of the safest chemicals as it breaks down into oxygen and water," says Kouk, "and you can't say that about a lot of chemicals."

Theoretically, hydrogen peroxide can completely decompose organic compounds into carbon dioxide and water. The amount of hydrogen peroxide needed to complete this stoichiometric reaction may not be eco-

nomically feasible, critics say. However, by using lesser amounts, organics can sometimes be decomposed into less toxic or more readily biodegradable by-products. Therefore, hydrogen peroxide can be useful as a pretreatment step before biological treatment to reduce toxicity, or as a tertiary treatment to remove remaining refractory organics.

Producers look to the development of new hydrogen peroxide-based technologies for industrial waste treatment as an area with strong growth potential. Both FMC and Interlox work with smaller companies to develop advanced treatment technologies based on hydrogen peroxide. These generally involve activating the hydrogen peroxide to more effectively break down organics, such as phenols, aromatics, and pesticides, which are coming under increasingly strict regulation by EPA.

"As the nature of the problems has gotten more complex," explains Randy Bull, manager of commercial development for FMC's Peroxygen Chemicals Division, "we've had to work at developing new and more complex technologies to address them." Hydroxyl radicals are produced in solution, a single radical can be created using a transition-metal catalyst. The oxidation reaction can be controlled or made selective to specific contaminants by changes in pH, temperature, concentration, retention times, and the presence of catalysts.

A newly developed technology employs an additional oxidant, such as ozone, and activation by UV light to produce two hydroxyl radicals and break down refractory organics. Hydrogen peroxide enhances the effectiveness of the ozone oxidation process, Bull says. "This technology is attractive since it does not require adding anything [but ozone and hydrogen peroxide] to the water." Hydrogen peroxide is also finding application as a source of dissolved oxygen in biological treatment and in bioremediation of groundwater.

Despite the growing need, questions still remain as to whether the technologies exist to deal with the stricter effluent and drinking water

standards proposed by EPA. "The most recent regulations are going to have us treating water for the removal of contaminants or pollutants that we've never treated for before," says Robert Bates, vice president and south region manager with Hart Environmental Management of New York City. "Some of the chemicals that have traditionally been used and conventional processes may diminish in use as new technologies are developed," he says, "because they don't do a particularly good job in removing the contaminants of concern."

Complying with water quality standards will have an impact on municipal and industrial water treatment operations as EPA regulations go into effect in the next few years. With the organic chemicals, plastics, and synthetic fibers guidelines being upheld in March 1989, industry must comply with pretreatment standards in three years and with direct discharge regulations when permits are renewed. Meeting standards of parts per million or parts per billion levels on more than 100 contaminants will require the investment of time and money on the part of industry and public treatment facilities. Increased monitoring and specialized treatments for previously unregulated chemicals will be the responsibility of companies or municipalities discharging water. To service customers, water treatment and specialty manufacturers will need to invest in research and development to develop advanced treatment methods.

The guidelines are expected to affect 1000 plants, according to EPA. In challenging the guidelines, the Chemical Manufacturers Association and the Synthetic Organic Chemicals Manufacturers Association focused on the economic and technical feasibility of meeting the proposed standards. The impact is expected to be disproportionately severe for smaller producers, which, without the economies of scale, may be put out of business. In 1987 when the guidelines were first issued, it was estimated that 60 plants might possibly be shut down and overall compliance costs would exceed \$500 million. □



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